

CLAIMS

1. Process for coating a composite material
5 consisting of electrically conductive or semiconductive
metal areas, and electrically non-conductive areas, the
said process comprising at least one step of
electroless growth of a metal layer plumb with the said
10 electrically conductive or semiconductive metal areas,
characterized in that the electrically non-conductive
areas of the composite material are not formed from
organic polymers and in that, prior to the said
electroless growth step, the said process furthermore
15 includes at least one first step of forming a
nucleation layer by covalent or dative grafting of an
organic or organometallic film on, and only on, the
said electrically conductive or semiconductive metal
areas, by bringing the said composite material into
20 contact with a solution of organic or organometallic,
difunctional precursors of the following formula (I):



in which:

- A is a group having at least one reactive
chemical function allowing the said organic precursor
25 to be covalently and selectively attached to the
surface of the said electrically conductive areas;

- X is a spacer arm covalently linked to A and
to B;

- n is an integer equal to 0 or 1; and

30 - B is a group having at least one ligand
function for metal ions or for metal aggregates, that
is to say allowing the complexation of metal ions
and/or metal aggregates.

35 2. Process according to Claim 1, characterized in
that the film has a thickness of between 1 and 100 nm.

3. Process according to Claim 2, characterized in
that the film has a thickness of between 1 and 10 nm.

4. Process according to any one of the preceding claims, characterized in that it furthermore includes a mordanting second step during which the organic or organometallic film formed on the electrically conductive or semiconductive metal areas is brought into contact with a mordanting solution comprising either at least one precursor of a metallic material or at least one precursor of a catalyst for its deposition, the said second step being carried out at the same time as or after the first step of forming the organic or organometallic film.

5. Process according to any one of the preceding claims, characterized in that it furthermore includes, before the step of electroless growth of the metal layer is carried out, a third step that consists in reducing the said organometallic compound of formula (I) and/or the said precursor of the metallic material or the precursor of a catalyst for its deposition as a metallic material, or as a catalyst for its deposition, respectively.

6. Process according to any one of the preceding claims, characterized in that the reactive function of the groups A of the difunctional, organic or organometallic, precursors of formula (I) is chosen from functions carrying lone pairs, radicals obtained from cleavable functions, carbocations and carbanions.

7. Process according to Claim 6, characterized in that the cleavable functions are chosen from disulphide, diazonium, sulphonium, iodonium and ammonium functions and alkyl or aryl iodides.

8. Process according to Claim 6, characterized in that the said reactive function of the groups A is a function carrying lone pairs chosen from amine, pyridine, thiol, ester, carboxylic acid, hydroxamic

acid, thiourea, nitrile, salicylic, amino acid and triazine functions.

9. Process according to any one of the preceding
5 claims, characterized in that X is chosen from: linear
or branched alkane chains; the phenylene group (-C₆H₄-);
phenylene groups substituted with electron-withdrawing
or electron-donating groups; groups carrying several
10 fused aromatic rings, which are themselves optionally
substituted with one or more electron-donating or
electron-withdrawing groups; and structures consisting
of combinations of these groups.

10. Process according to any one of the preceding
15 claims, characterized in that the ligand functions
defined as regards part B of the difunctional
precursors of formula (I) are chosen from amines,
amides, pyridines, nitriles, amino acids, triazines,
bipyridines, terpyridines, quinolines,
20 orthophenanthroline compounds, ethers, carbonyls,
carboxyls and carboxylates, esters, hydroxamic acids,
salicylic acids, phosphines, phosphine oxides, thiols,
thioethers, disulphides, ureas, thioureas, crown
ethers, aza-crown compounds, thio-crown compounds,
25 cryptands, sepulcrates, podands, porphyrins,
calixarenes, naphthols, isonaphthols, siderophores,
antibiotics, ethylene glycol and cyclodextrins;
substituted and/or functionalized molecular structures
based on these functional groups; and their metal
30 complexes with one or more metal ions or metal
aggregates.

11. Process according to any one of the preceding
claims, characterized in that the compounds of formula
35 (I) are chosen from: aryldiazonium salts functionalized
in the para position of the diazonium group by a ligand
function, optionally via a spacer arm X; alkyl or aryl
iodides functionalized by a ligand function;
bipyridines; aminothiols; diamines and

polyethyleneimine; it being understood that, in these compounds, the said ligand function is as defined in Claim 1 or 10.

5 12. Process according to Claim 11, characterized in that the aryldiazonium salts functionalized in the para position of the diazonium group by a ligand function are chosen from 4-ethylammoniumphenyldiazonium tetrafluoroborate, 4-(2-aminoethyl)benzenediazonium ditetrafluoroborate, 4-cyanobenzenediazonium tetrafluoroborate, 4-carboxy-3-hydroxybenzenediazonium tetrafluoroborate, 3-carboxy-4-nitrobenzenediazonium tetrafluoroborate, 4-carboxybenzenediazonium tetrafluoroborate and 4-thioethanolphenyldiazonium tetrafluoroborate.

15 13. Process according to Claim 11, characterized in that the aminothiols are chosen from cysteamine, aminopropanethiol, aminohexanethiol and sulphur-containing amino acids.

20 14. Process according to Claim 11, characterized in that the diamines are chosen from ethylenediamine and hexamethylenediamine.

25 15. Process according to any one of the preceding claims, characterized in that the said composite material is brought into contact with the solution of difunctional precursors by immersion, by spin coating or by spraying.

30 16. Process according to any one of the preceding claims, characterized in that the surface of the composite material consists of an alternation of copper tracks with a width of L, separated from the dielectric tracks.

35 17. Process according to Claim 16, characterized in that the width L is between 150 and 30 nm.

18. Process according to any one of Claims 4 to 17, characterized in that the precursors of the metallic material that serve for the nucleation layer and are used in the mordanting solution during the second step
5 are metal ions chosen from copper, zinc, gold, tin, titanium, vanadium, chromium, iron, cobalt, lithium, sodium, aluminium, magnesium, potassium, rubidium, caesium, strontium, yttrium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, cadmium, indium,
10 lutecium, hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, mercury, thallium, lead and bismuth ions, ions of the lanthanides and of the actinides, and mixtures thereof.

15 19. Process according to Claim 18, characterized in that the concentration of metal ions in the mordanting solution is less than $10^{-4}M$.

20 20. Composite material comprising at least one surface consisting of an alternation of electrically conductive or semiconductive areas and electrically non-conductive areas, which can be obtained by implementing the process as defined in any one of Claims 1 to 18, characterized in that the electrically non-conductive
25 areas of the composite material are not formed from organic polymers and in that the electrically conductive or semiconductive areas are covered with a nucleation layer grafted covalently or datively and consisting of difunctional, organic or organometallic
30 compounds of the following formula (I)



in which:

- A is a group having at least one reactive chemical function allowing the said organic precursor
35 to be covalently and selectively attached to the surface of the said electrically conductive areas;

- X is a spacer arm covalently linked to A and to B;

- n is an integer equal to 0 or 1; and

- B is a group having at least one ligand function for metal ions or for metal aggregates, that is to say allowing the complexation of metal ions and/or metal aggregates,

5 the said film itself being coated with a layer of a metallic material.

21. Process for fabricating interconnects in microelectronics, electronic microsystems or integrated
10 circuits, characterized in that it includes at least one step of grafting a film of difunctional precursors of formula (I) using the coating process as defined in any one of Claims 1 to 19, the said interconnects being made of a metallic material.

15 22. Process according to Claim 21, characterized in that it comprises, in the following order, the steps consisting in:

20 a) etching interconnect features in a dielectric substrate, the said features forming trenches and/or vias, and optionally projections, on and/or through the said substrate,

25 b) depositing a conductive barrier layer on the said etched dielectric substrate, which barrier layer prevents the migration of the interconnect metallic material into the said substrate, the said barrier layer having a thickness such that the free face of this layer conformally follows the interconnect features of the said substrate on which it is
30 deposited;

 c) coating the conductive barrier layer deposited on the etched substrate with a nucleation film of a metallic material;

35 d) filling the trenches and/or vias with the said metallic material starting from the said nucleation film, in order to form the said metal interconnects made of the said metallic material;

 e) uniformly and homogeneously abrading the surface, for a time sufficient to cut off the

protruding parts of the said etched features, in order to obtain a copper/dielectric composite surface;

5 f) activating the said composite surface using the process and as defined in any one of Claims 1 to 19 via the deposition of an organic or inorganic film grafted onto and self-positioned with respect to the conductive copper lines of the composite surface; and

10 g) using the said film as a catalytic layer or nucleation layer for the electroless growth of a metal layer as a copper diffusion barrier, the said metal layer being self-positioned with respect to the copper conductive areas of the composite surface.

23. Use of the process of Claim 21 or 22 for the
15 fabrication of interconnect elements in microelectronics, of electronic microsystems or of integrated circuits.

24. Interconnect elements in microelectronics,
20 electronic microsystems and integrated circuits that can be obtained by implementing the process of claim 21 or 22.